In J Phys. 77B (3), 291-297 (2003)

AN INTERNATIONAL JOURNAL
IJP B

# Quantum corrections to equation of state of fluid mixtures of hard non-spherical molecules

T K Dey[1], S C Singh[2] and S K Sinha[3]*

[1] Department of Physics, Government Mahila Inter College, Purnia-854 301, Bihar, India

[2] Department of Physics, Patna Collegiate, Patna-800 004, Bihar, India

[3] Department of Physics, L S College, B B. A. Bihar University, Muzaffarpur-842 001, Bihar, India

*Received 25 November 2002, accepted 3 March 2003*

Abstract The expression for the leading quantum correction to the third virial coefficient and equation of state of the fluid mixture of the hard Gaussian overlap molecules are given The numerical results are discussed under the conditions of (i) $\sigma_{11}^0 = \sigma_{22}^0$ and (ii) $\nu_1 = \nu_2$ The quantum effects depend on the conditions and relative values of the shape parameters K in general and increase with the packing fraction $\eta$ in particular .

Keywords Quantum corrections, fluid mixtures, Gaussian overlap molecules

PACS Nos. 05.70.Ce, 61.25.Em, 64.10.+h

## Introduction

The purpose of the present work is to develop a theory for calculating the quantum correction to the thermodynamic properties of fluid mixture of hard non-spherical molecules. The Gaussian overlap ( HGO ) model has been widely used for molecular fluid of hard non-spherical molecules [1]. This is because of the HGO model has a close connections with the hard ellipsoid of revolution (HER ) and is a useful reference system for molecular fluids of non-spherical molecules.

In the semiclassical limit ( *i e*, at high temperature) where the quantum effects are small and treated as correction to the classical behaviour, the hard convex bodies can be dealt with the Hemmer -Jancovici (HJ) method [2] . Singh *et al* [3] have employed this method to calculate the leading quantum correction to the thermodynamic properties of the HER fluid. Kumari and Sinha [4] have extended theory for the mixture and calculated the quantum corrections to the second virial coefficient and free energy for the HGO fluid mixtures.

Corresponding Author

Address for correspondence : Ramani Mohan Garden, Kalambag Road Chowk, Muzaffarpur-842 002, Bihar, India.

In the present paper, we calculate the classical and quantum correction values of the third virial coefficient and equation of state of the HGO fluid mixtures

## 2. Basic theory

We consider a fluid mixture of non-spherical molecules interacting *via* the hard Gaussian overlap ( HGO ) potential defined as

$$u_{\alpha\beta}(r\omega_1\omega_2) = \infty \quad , \quad r < \sigma_{\alpha\beta}(\omega_1\omega_2) ,$$

$$= 0 \quad , \quad r > \sigma_{\alpha\beta}(\omega_1\omega_2) , \qquad (1)$$

where $\sigma_{\alpha\beta}(\omega_1\omega_2)$ is the distance of closest approach between two hard – core molecules of species $\alpha$ and $\beta$, $r = |r_1 - r_2|$ is the centre -to-centre distance and $\omega_i$ is the orientational coordinate of molecule $i$, $\sigma_{\alpha\beta}(\omega_1\omega_2)$ can be expressed in terms of the Euler angles [4, 5] as

$$\sigma_{\alpha\beta}(\omega_1\omega_2) = \sigma_{\alpha\beta}^0 \Big[ 1 - \chi_{\alpha\beta} \Big( \cos^2\theta_1 + \cos^2\theta_2 - 2\chi_{\alpha\beta} \cos\theta_1 \cos\theta_2 \cos\theta_{12} \Big) / \Big( 1 - \chi_{\alpha\beta}^2 \cos^2\theta_{12} \Big) \Big]^{-1/2} , \qquad (2)$$

where $\sigma^0_{\alpha\beta}$ is the width and $\chi_{\alpha\beta}$ the shape parameter defined as

$$\chi_{\alpha\beta} = \left(K^2_{\alpha\beta} - 1\right)/\left(K^2_{\alpha\beta} + 1\right), \tag{3}$$

$K_{\alpha\beta}$ being the length-to-breadth ratio of the molecule . The effective values of $\sigma^0_{12}$ and $K_{12}$ between the HGO molecules of unlike species can be given by [3, 4]

$$\sigma^0_{12} = \left(\sigma^0_{11} + \sigma^0_{22}\right)/2, \tag{4a}$$

$$K_{12} = \left(K_{12}\sigma^0_{11} + K_{22}\sigma^0_{22}\right)/\left(\sigma^0_{11} + \sigma^0_{11}\right). \tag{4b}$$

The free energy of the HGO fluid mixture correct to the first order quantum correction, is written as [ 4 ]

$$A/NkT = A^c/NkT - (1/2)\,\rho \sum_{\alpha\beta} \chi_\alpha \chi_\beta \int dr < g^c_{\alpha\beta}(r\omega_1\omega_2)$$

$$U^m_{\alpha\beta}(r\omega_1\omega_2) >_{\omega_1\omega_2} + 0\left(\lambda^2_{\alpha\beta}\right), \tag{5}$$

where $A^c$ and $g^c_{\alpha\beta}(r\omega_1\omega_2)$ are , respectively , the free energy and pair distribution function ( PDF ) of the classical hard convex body (HCB ) fluid mixture, $\rho = N/V$ is the number density and $\chi_\alpha = N_\alpha / N$ is the concentration of species $\alpha$ ( $N$ is the total number of molecules and $V$ the volume of the system) Here, $U^m_{\alpha\beta}(r\omega_1\omega_2)$ is the 'modified' Ursell function of the hard-body mixture and $< (\ldots) >_{\omega_1\omega_2}$ represents an unweighted average over the molecular orientations $\omega_1$ and $\omega_2$ for the quantity within the angular bracket *i.e*,

$$< (\ldots) >_{\omega_1\omega_2} = (4\pi)^{-2} \int d\omega_1 \int d\omega_2 (\ldots). \tag{6}$$

Other thermodynamic properties can be obtained from the free energy. Thus, the equation of state is given by

$$P/\rho kT = P^c/\rho kT - (1/2)\rho \sum_{\alpha\beta} \chi_\alpha \chi_\beta \int dr < \left[g^c_{\alpha\beta}(r\omega_1\omega_2)\right.$$

$$\left. + \rho \partial g^c_{\alpha\beta}(r\omega_1\omega_2)/\partial\rho\right] U^m_{\alpha\beta}(r\omega_1\omega_2) >_{\omega_1\omega_2} + 0\left(\lambda^2_{\alpha\beta}\right), \tag{7}$$

where $P^c$ is the pressure of classical HCB fluid mixture and given by [6]

$$\frac{P^c}{\rho kT} = \frac{1}{(1-\eta)} + \frac{rs}{\rho(1-\eta)^2} + \left[qs^2(1-2\eta) + 5rs\eta^2\right]/(1-\eta)^3, \tag{8}$$

where

$$\eta = \rho(x_1 v_{11} + x_2 v_{22}), \tag{9}$$

and $r, q$ and $s$ are geometric quantities of a mixture defined as

$$r = \sum_\alpha \rho_\alpha R_\alpha - \rho \sum_\alpha \chi_\alpha R_\alpha ,$$

$$q = \sum_\alpha \rho_\alpha R_\alpha{}^2 = \rho \sum \chi_\alpha R_\alpha{}^2 ,$$

$$s = \sum_\alpha \rho_\alpha \xi_\alpha = \rho \sum_\alpha \chi_\alpha \xi_\alpha . \tag{10}$$

Here, $R_\alpha$ is the $(1/4\pi)$ – multiple of the mean curvature integral , $\xi_\alpha$ the surface integral and $v_\alpha$ is the volume of the HCB molecule of species $\alpha$ .

## 3. Virial equation of state of dilute hard Gaussian overlap fluid mixtures

The PDF of the classical fluid mixture can be expanded in power of $\rho$ as [ 7 ]

$$g^c_{\alpha\beta}(r_{12}\omega_1\omega_2) = \exp\left[-\beta u_{\alpha\beta}(r_{12}\omega_1\omega_2)\right]$$

$$\left[1 + \rho \sum_r x_r a^{c(1)}{}_{\alpha\gamma\beta}(r_{12}\omega_1\omega_2) + \ldots\ldots\right], \tag{11}$$

where the coefficient $a^{c(1)}{}_{\alpha\gamma\beta}(r_{12}\omega_1\omega_2)$ is the cluster integral involving one field point and two base points. Substituting eq (11)in eq. (7), one can expresss the equation of state in the virial form *i.e* in power of $\rho$

$$P/\rho kT = A + B\rho + C\rho^2 + .$$

where $A = 1$, $B$ and $C$ are the second and third virial coefficients respectively . They can be expressed as

$$B = B^c - (1/2)\sum_{\alpha\beta} \chi_\alpha \chi_\beta \int dr < \exp\left[-\beta u_{\alpha\beta}(r\omega_1\omega_2)\right]$$

$$\times U^m_{\alpha\beta}(r\omega_1\omega_2) >_{\omega 1 \omega 2}$$

$$C = C^c - \sum_{\alpha\beta\gamma} \chi_\alpha \chi_\beta \chi_\gamma \int dr_2 < \exp\left[-\beta u_{\alpha\beta}(r_{12}\omega_1\omega_2)\right]$$

$$\times a^{c(1)}_{\alpha\gamma\beta}(r_{12}\omega_1\omega_2) U^m_{\alpha\beta}(r_{12}\omega_1\omega_2) >_{\omega_1\omega_2}, \tag{14}$$

where $B^c$ and $C^c$ are, respectively, second and third virial coefficients of classical HCB fluid mixture.Expanding eq. (8), in power of $\rho$ , one gets

$$B^c = \sum_{\alpha,\beta} \chi_\alpha \chi_\beta B^c_{\alpha\beta} \tag{15}$$

with

$$B^c_{\alpha\beta} = (1/2)\left[v_\alpha + v_\beta + R_\alpha \xi_\beta + R_\beta \xi_\alpha\right] \tag{16}$$

and

$$C^c = \sum_{\alpha\beta\gamma} \chi_\alpha \chi_\beta \chi_\gamma C^c_{\alpha\beta\gamma} \tag{17}$$

with

$$C^c_{\alpha\beta\gamma} = (1/3)\left(\left[v_\alpha v_\beta + v_\beta v_\gamma + v_\alpha v_\gamma\right] + \left[v_\alpha\left(R_\beta \xi_\gamma + R_\gamma \xi_\beta\right)\right.\right.$$

$$+\nu_\beta\left(R_\gamma\xi_\alpha + R_\alpha\xi_\gamma\right)+\nu_\gamma\left(R_\alpha\xi_\beta + R_\beta\xi_\alpha\right)\Big]$$

$$+(1/3)\Big[R_\alpha^2\xi_\beta\xi_\gamma + R_\beta^2\xi_\gamma\xi_\alpha + R_\gamma^2\xi_\alpha\xi_\beta\Big]\Big). \qquad (18)$$

Eq ( 18 ) is identical to that derived by Boublik and Nezbeda [6] The second virial coefficient of the HGO fluid mixture is studied earlier [ 4 ] .

In this paper, we calculate the quantum correction to the third virial coefficient. For the HGO mixture, eq. ( 14 ) reduces to

$$C = C^{c} + \Sigma_{\alpha,\beta,\gamma}\, \chi_\alpha\, \chi_\beta\chi_\gamma C_{\alpha\beta\gamma}{}^{qc}, \qquad (19)$$

where

$$C_{\alpha\beta\gamma}{}^{qc} = -(1/3)\int dr_2 < a_{\alpha\gamma\beta}{}^{c(1)}(r_{12}\omega_1\omega_2)$$

$$\times U^{m}_{\alpha\beta}(r_{12}\omega_1\omega_2) + a_{\alpha\beta\gamma}{}^{c(1)}(r_{12}\omega_1\omega_2)\, U^{m}_{a\gamma}(r_{12}\omega_1\omega_2)$$

$$+a'_{\beta\alpha\gamma}{}^{(1)}(r_{12}\omega_1\omega_2)U^{m}_{\beta\gamma}(r_{12}\omega_1\omega_2) >_{\omega_1\omega_2}. \qquad (20)$$

In order to evaluate the quantum correction terms, we introduce a reduced variable $r^* = r/\sigma_{\alpha\beta}(\omega_1\omega_2)$ , then the HGO potential ( eq . (1)) reduces to the central hard sphere (HS) potential Consequently, the cluster integral of the classical HGO fluid mixture becomes that of the classical HS fluid mixture *i.e.*

$$a^{c(1)}{}_{\alpha\gamma\beta}(r\,\omega_1\,\omega_2) = a^{cHS}{}_{\alpha\gamma\beta}(r^*), \qquad (21)$$

where $a^{cHS}{}_{\alpha\gamma\beta}(r^*)$ is the cluster integral of the classical HS fluid mixture of the effective diameter $d_{\alpha\beta} = K^{1/3}{}_{\alpha\beta}\sigma^{0}{}_{\alpha\beta}$. An analytic expression for $a^{cHS}{}_{\alpha\gamma\beta}(r)$ is given by [8]

$$a^{cHS}{}_{\alpha\gamma\beta}(r) = (2\pi/3)\Big[\left(d^3_{\alpha\gamma} + d^3_{\beta\gamma}\right) - (3/4)\left(d^3_{\alpha\gamma} + d^3_{\beta\gamma}\right)r$$

$$+(1/8)r^3 - (3/8)\left(d^2_{\alpha\gamma} - d^2_{\beta\gamma}\right)^2/r\Big],$$

for $d_{\alpha\beta} < r \le d_{\alpha\gamma} + d_{\beta\gamma}$ ;

$= 0$, for $r > d_{\alpha\gamma} + d_{\beta\gamma}$ . (22)

In this approach , the ' modified' Ursell function $u^{m}_{\alpha\beta}(r\,\omega_1\,\omega_2)$ of the HGO fluid mixture is

$$U^{m}_{\alpha\beta}(r\,\omega\omega) = U^{m}_{\alpha\beta}\left(r/\sigma_{\alpha\beta}(\omega_1\,\omega_2)\right) \qquad (23)$$

$$= U^{m}_{\alpha\beta,HS}(r^*),$$

where $U^{m}_{\alpha\beta,HS}(r^*)$ is the 'modified' Ursell function of the HS fluid mixture and is given by [3 ]

$$U^{m}_{\alpha\beta,HS}(r^*) = -\left(\lambda_{\alpha\beta}/\sigma_{\alpha\beta}(\omega_1\omega_2)\right)\delta(r^*-1) + 0(\lambda^2_{\alpha\beta}). \qquad (24)$$

Here, $\delta(r^*-1)$ is the Dirac -delta function and $\lambda_{\alpha\beta}$ is the thermal wavelength of the molecule of species $\alpha$ and $\beta$ defined as

$$\lambda_{\alpha\beta} = (2\pi\hbar^2\beta/m_{\alpha\beta})^{1/2}, \qquad (25)$$

where $m_{\alpha\beta} = 2m_{\alpha\alpha}m_{\beta\beta}/(m_{\alpha\alpha} + m_{\beta\beta})$ and $m_{\alpha\alpha} = m_\alpha$ is the mass of the molecule of species $\alpha$ . Substituting eqs. (21)-(25) in eq. (20) ,we obtain an analytic expression for $C^{qc}{}_{\alpha\beta\gamma}$ as

$$C^{qc}{}_{\alpha\beta\gamma} = (\pi^2/54)(3/\sqrt{2})\Big\{F^1_{\alpha\beta}\left(\lambda_{\alpha\beta}/\sigma^0_{\alpha\beta}\right)\Big[d^6_{\alpha\beta}$$

$$-6d^4_{\alpha\beta}\left(d^2_{\alpha\gamma} + d^2_{\beta\gamma}\right) + 8d^3_{\alpha\beta}\left(d^3_{\alpha\gamma} + d^3_{\beta\gamma}\right)$$

$$-3d^2_{\alpha\beta}\left(d^2_{\alpha\gamma} - d^2_{\beta\gamma}\right)^2\Big] + F^1_{\alpha\gamma}\left(\lambda_{\alpha\lambda}/\sigma^0_{\alpha\gamma}\right)$$

$$\Big[d^6_{\alpha\gamma} - 6d^4_{\alpha\gamma}\left(d^2_{\alpha\beta} + d^2_{\beta\gamma}\right) + 8d^3_{\alpha\gamma}\left(d^3_{\alpha\beta} + d^3_{\beta\gamma}\right)$$

$$-3d^2_{\alpha\gamma}\left(d^2_{\alpha\beta} - d^2_{\beta\gamma}\right)^2\Big] + F^1_{\beta\gamma}\left(\lambda_{\beta\gamma}/\sigma^0_{\beta\gamma}\right)$$

$$\Big[d^6_{\beta\gamma} - 6d^4_{\beta\gamma}\left(d^2_{\alpha\beta} + d^2_{\beta\gamma}\right) + 8d^3_{\beta\gamma}\left(d^3_{\alpha\beta} + d^3_{\alpha\gamma}\right)$$

$$-3d^2_{\beta\gamma}\left(d^2_{\alpha\beta} - d^2_{\alpha\gamma}\right)^2\Big]\Big\} + O\left(\lambda^2_{\alpha\beta}\right), \qquad (26)$$

where we assumed that $d_{\alpha\beta} = K^{1/3}_{\alpha\beta}\sigma^0_{\alpha\beta}$ and [4]

$$K_{\alpha\beta}F^1{}_{\alpha\beta}(K_{\alpha\beta}) = \left\langle D_{\alpha\beta}(\omega_1\omega_2)\right\rangle, \qquad (27a)$$

$$D_{\alpha\beta}(\omega_1\omega_2) = (4\pi)^{-1}\int d\hat{r}\left(\sigma_{\alpha\beta}(\omega_1\omega_2)/\sigma^0{}_{\alpha\beta}\right)^2. \qquad (27b)$$

The values of $F^1_{\alpha\beta}$ can be obtained as a function $K_{\alpha\beta}$ from Eq. (27a) [4].

We evaluate the quantum corrections to the third virial coefficient for the HGO mixture . We assume that the molecular mass $m_\alpha$ is proportional to the volume $v_\alpha$ (*i.e* , proportional to $K_{\alpha\alpha}\sigma^{03}{}_{\alpha\alpha}$ in case of the HGO molecule ) . Thus from eq . (25) , we have [4]

$$\lambda_{22}/\sigma^0_{22} = (K_{11}/K_{22})^{1/2}R^{-5/2}(\lambda_{11}/\sigma^0_{11}), \qquad (28)$$

$$\lambda_{22}/\sigma^0_{22} = \sqrt{2}\left[1 + (K_{11}/K_{12})R^{-3}\right]^{1/2}(\lambda_{11}/\sigma^0_{11})/(1+R), \qquad (29)$$

where $R = \sigma^0_{22}/\sigma^0_{11}$.

From eq. (26) and with the help of eqs. (28) and (29), we obtain expressions for $C^{qc}_{\alpha\beta\gamma}$ in simple form

$$C^{qc}_{111} = (3/\sqrt{2})A^1_{111}\left(\lambda_{11}/\sigma^0_{11}\right), \tag{30a}$$

$$C^{qc}_{112} = (3/\sqrt{2})A^1_{112}\left(\lambda_{11}/\sigma^0_{11}\right), \tag{30b}$$

$$C^{qc}_{122} = (3/\sqrt{2})A^1_{122}\left(\lambda_{11}/\sigma^0_{11}\right), \tag{30c}$$

$$C^{qc}_{222} = (3/\sqrt{2})A^1_{222}\left(\lambda_{11}/\sigma^0_{11}\right), \tag{30d}$$

where $A^1$ is the first order quantum correction coefficient for the third virial coefficient .They are expressed as

$$A^1_{111} = \left(5\pi^2/18\right)\left(K_{11}\sigma^{03}_{11}\right)^2 F^1_{11}, \tag{31a}$$

$$A^1_{112} = \left(\pi^2/54\right)\left(K_{11}\sigma^{03}_{11}\right)^2\left(F^1_{11}\left[1-12L^{2/3}+16L\right]\right.$$
$$\left.+2F^1_{12}\left[8L-3L^{2/3}\right]a_{12}\right), \tag{31b}$$

$$A^1_{122} = \left(\pi^2/54\right)\left(K_{22}\sigma^{03}_{22}\right)^2\left(F^1_{22}\left[1-12M^{2/3}+16M\right]a_{22}\right.$$
$$\left.+2F^1_{12}\left[8M-3M^{2/3}\right]a_{12}\right), \tag{31c}$$

$$A^1_{222} = \left(5\pi^2/18\right)\left(K_{12}\sigma^{03}_{22}\right)^3 F^1_{22}a_{22}, \tag{31d}$$

where

$$a_{22} = \left(K_{11}/K_{22}\right)^{1/2} R^{-5/2}, \tag{32a}$$

$$a_{12} = \sqrt{2}\left[1+\left(K_{11}/K_{22}\right)R^{-3}\right]^{1/2}/(1+R) \tag{32b}$$

and

$$L = \left(K_{12}/K_{11}\right)\left(\sigma^0_{12}/\sigma^0_{11}\right)^3, \tag{33a}$$

$$M = \left(K_{11}/K_{22}\right)\left(\sigma^0_{12}/\sigma^0_{22}\right)^3 = L\left(K_{11}/K_{22}\right)\left(\sigma^0_{11}/\sigma^0_{22}\right)^3 \tag{33b}$$

Finally, the third virial coefficient $C_{\alpha\beta\gamma}$ for the HGO mixture correct to the first order quantum correction , is expressed as

$$C_{\alpha\beta\gamma} = C^c_{\alpha\beta\gamma} + (3/\sqrt{2})\,A^1_{\alpha\beta\gamma}\left(\lambda_{11}/\sigma^0_{11}\right). \tag{34}$$

We first calculate the classical third coefficient for the HGO mixture using eq.(18). They are compared with the exact simulation results [6] in Table 1. The agreement is fairly good. In Table 2, we compare the third virial coefficient $C_{\alpha\beta\gamma}/\sigma^{06}_{12}$ for the HGO mixture at $\lambda_{11}/\sigma^0_{11} = 0.1$ with the classical values $C^c_{\alpha\beta\gamma}$ (where $\lambda_{11}/\sigma^0_{11} = 0.0$). The quantum correction increases the virial coefficient.

We are also interested in this paper in estimating the excess third virial coefficient of the HGO mixture (relative to the pure

**Table 1.** Comparison of the classical third virial coefficient $C^c_{\alpha\beta\gamma}/\sigma^{06}_{12}$ for the mixture of the hard Gausian overlap molecule with exact results

| Condition | $K_{11}/K_{22}$ | $C^c_{111}/\sigma^{06}_{12}$ | | $C^c_{112}/\sigma^{06}_{12}$ | | | | $C^c_{222}/\sigma^{06}_{12}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | Theory | Exact | Theory | Exact | Theory | Exact | Theory | Exact |
| $\sigma^0_{11}/\sigma^0_{22}$ | 1.792/1.0 | 10.17 | 10.64 | 6.42 | 6.82 | 4.05 | 4.34 | 2.74 | 2.74 |
| | 1.792/1.436 | 10.17 | 10.64 | 8.47 | 8.78 | 7.19 | 7.22 | 5.98 | 5.93 |
| $\nu_1 = \nu_2$ | 1.792/1.0 | 5.52 | 5.77 | 5.26 | 5.43 | 5.00 | 5.08 | 4.78 | 4.78 |
| $\nu_1 = (2/3)\nu_2$ | 1.79/1.0 | 3.49 | 3.65 | 4.44 | 4.54 | 5.39 | 5.57 | 6.79 | 6.79 |

**Table 2.** The third virial coefficient $C_{\alpha\beta\gamma}/\sigma^{06}_{12}$ for the mixture of the hard Gausian overlap molecules for $\lambda_{11}/\sigma^0_{11} = 0.0$ and 0.1 $\lambda_{11}/\sigma^0_{11} = 0.0$ corresponds $C^c_{\alpha\beta\gamma}$

| Condition | $K_{11}/K_{22}$ | $C^c_{111}/\sigma^{06}_{12}$ | | $C^c_{112}/\sigma^{06}_{12}$ | | $C^c_{122}/\sigma^{06}_{12}$ | | $C^c_{222}/\sigma^{06}_{12}$ | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\lambda_{11}/\sigma^0_{11}$ | | $\lambda_{11}/\sigma^0_{11}$ | | $\lambda_{11}/\sigma^0_{11}$ | | $\lambda_{11}/\sigma^0_{11}$ | |
| | | 0.0 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 | 0.0 | 0.1 |
| $\sigma^0_{11}/\sigma^0_{22}$ | 1.792/1.0 | 10.17 | 10.94 | 6.42 | 7.06 | 4.05 | 4.50 | 2.74 | 3.11 |
| | 1.792/1.436 | 10.17 | 10.94 | 8.47 | 9.17 | 7.19 | 7.80 | 5.98 | 6.56 |
| | 1.792/1.0 | 5.52 | 5.93 | 5.26 | 5.71 | 5.00 | 5.44 | 4.78 | 5.17 |

components). From eqs.(17) and (19), the excess third virial coefficient of the HGO mixture is obtained as

$$\Delta C = 3\chi_1\chi_2\Big[\big(\chi_1 C^c_{112} + \chi_2 C^c_{122}\big) + \big(3/\sqrt{2}\big) \times \big(\chi_1 A^1_{112} + \chi_2 A^1_{122}\big)\big(\lambda_{11}/\sigma^0_{11}\big)\Big]. \quad (35)$$

In order to simplify eq. (35), we introduce the following quantities.

$$\sigma^{03}K = \chi_1\sigma^{03}_{11}K_{11} + \chi_2\sigma^0_{22}K_{22}, \quad (36a)$$

$$\sigma^{02}K\lambda = \chi_1\sigma^{02}_{11}K_{11}\lambda_{11} + \chi_2\sigma^{02}_{22}K_{22}\lambda_{22}, \quad (36b)$$

From eq. (28),(36a) and (36b), we get

$$\lambda_{11}/\sigma^0_{11} = E_{11}\big(\lambda/\sigma^0\big), \quad (37)$$

where

$$E_{11} = \big(\chi_1 K_{11} + \chi_2 K_{22} R^3\big)/\big(\chi_1 K_{11} + \chi_2 (K_{11}/K_{22})^{1/2} R^{1/2}\big). \quad (38)$$

Then eq (35) can be expressed as

$$\Delta C = \Delta C^c + \big(3/\sqrt{2}\big)\Delta C^1\big(\lambda/\sigma^0\big), \quad (39)$$

where

$$\Delta C^c = 3\chi_1\chi_2\big(\chi_1 C^c_{112} + \chi_2 C^c_{122}\big), \quad (40a)$$

$$\Delta C^1 = 3\chi_1\chi_2\big(\chi_1 A^1_{112} + \chi_2 A^1_{122}\big)E_{11}. \quad (40b)$$

The excess third virial coefficient $\Delta C/\sigma^{06}_{12}$ of the HGO mixture is shown in Figure 1 for $\sigma^0_{11} = \sigma^0_{22}$ as a function of $\chi_1$ for $\lambda/\sigma^0 = 0.0$ and 0.1 .They are zero at $\chi_1 = 0.0$ and $\chi_1 = 1.0$ and finite in the intermediate range of $\chi_1$ .

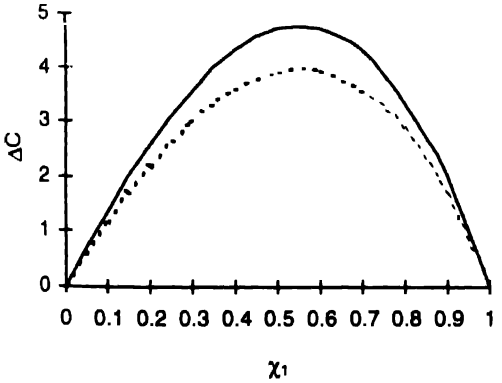


Figure 1. Excess third virial coefficient $\Delta C$ for the HGO fluid mixture for $K_{11}/K_{22}$ =1 792/1.0 at $\lambda/\sigma^0 = 0.0$ and 0.1. The thick line represents $\lambda/\sigma^0$ = 0 1 and dotted line $\lambda/\sigma^0$ = 0.0.

## 4. Equation of state of dense hard -Gaussian overlap fluid mixtures

Using the reduced variable $r^* = r/\sigma_{\alpha\beta}(\omega_1\omega_2)$ , the PDF $g^c_{\alpha\beta}(r\omega_1\omega_2)$ of the classical HGO fluid mixture reduces to that of classical HS mixture *i.e.*

$$g^c_{\alpha\beta}(r\omega_1\omega_2) = g^c_{\alpha\beta}\big(r/\sigma_{\alpha\beta}(\omega_1\omega_2)\big) = g^{CHS}_{\alpha\beta}(r^*). \quad (41)$$

Substituting eq. (24) in eq. (7) , we get

$$P/\rho kT = P^c/\rho kT + (\pi/\sqrt{2})\,\rho\sum_{\alpha\beta} x_\alpha x_\beta\Big[g^{CHS}_{\alpha\beta}(1) + \rho\,\partial g^{CHS}_{\alpha\beta}(1)/\partial\rho\Big]F^1_{\alpha\beta}K_{\alpha\beta}\sigma^{02}_{\alpha\beta}\lambda_{\alpha\beta} + O\big(\lambda^2_{\alpha\beta}\big), \quad (42)$$

where $P^c/\rho kT$ is given by eq. (8). The quantum correction term can be evaluated using the extended Van der Waals one (EvdW1) fluid theory of mixture [4] . This theory approximates the properties of mixture by those of a fictitious hard non-sphere fluid with parameters :

$$K_0 d_0^3 = \Sigma_{\alpha\beta}\,\chi_\alpha\,\chi_\beta\,K_{\alpha\beta}\sigma^{03}_{\alpha\beta}, \quad (43a)$$

$$K_0 d_0^2\lambda_0 = \Sigma_{\alpha\beta}\,\chi_\alpha\,\chi_\beta\,K_{\alpha\beta}\sigma^{02}_{\alpha\beta}\lambda_{\alpha\beta}, \quad (43b)$$

$$K_0 d_0\lambda_0 F^1(K_0) = \Sigma_{\alpha\beta}\,\chi_\alpha\,\chi_\beta\,K_{\alpha\beta}\sigma^{02}_{\alpha\beta}\lambda_{\alpha\beta}F^1_{\alpha\beta}. \quad (43c)$$

In the E v d W I theory of mixture , we further assume that

$$g^{CHS}_{\alpha\beta}(1) = g^{CHS}(d_0) \quad (44)$$

for all $\alpha,\beta$ where $g^{CHS}(d_0)$ is the classical radial distribution function ( RDF) of the hard sphere system at the core. Thus, eq. (42) reduces to a simple form :

$$P/\rho kT - P^c/\rho kT = \big(\pi/\sqrt{2}\big)\big(\rho K_0 d_0^3\big)\Big[g^{CHS}(d_0) + \rho\,\partial g^{CHS}_{\alpha\beta}(do)/\partial\rho\Big]F^1(K_0)(\lambda_0/d_0) + 0\big(\lambda_0^2\big). \quad (45)$$

From eqs. (43a) and (43b) and using eqs. (32) and (37) , we get

$$\lambda_0/d_0 = E\big(\lambda/\sigma^0\big), \quad (46)$$

where

$$E = \big(\chi_1^2 K_{11}\sigma^{03}_{11} + \chi_2^2 K_{22}\sigma^{03}_{22}a_{22} + 2\chi_1\chi_2 K_{12}\sigma^{03}_{12}a_{12}\big)/\big(\chi_1 K_{11}\sigma^{03}_{11} + \chi_2^2 K_{22}\sigma^{03}_{22} + 2\chi_1\chi_2 K_{12}\sigma^{03}_{12}\big)E_{11}. \quad (47)$$

Similarly, from eqs (43b) and (43 c), we get

$$F^1 = \big(\chi_1^2 K_{11}\sigma^{03}_{11}F^1_{11} + \chi_2^2 K_{22}\sigma^{03}_{22}F^1_{22}a_{22}$$

$$+2\chi_1\chi_2 K_{12}\sigma_{12}^{03}F_{12}^{1}a_{12}\Big)/\Big(\chi_1^2 K_{11}\sigma_{11}^{03}$$

$$+\chi_2^2 K_{22}\sigma_{22}^{03}a_{22}+2\chi_1\chi_2 K_{12}\sigma_{12}^{03}a_{12}\Big). \quad (48)$$

For the hard sphere fluid, $g^{CHS}(d_0)$ is given by [3]

$$g^{CHS}(d_0)=(1-\eta_0/2)/(1-\eta_0)^3, \quad (49)$$

where

$$\eta_0=(\pi/6)\rho K_0 d_0^3$$

which can be expressed as

$$\eta_0=\eta\Big[1+\chi_1\chi_2\Big(2K_{12}\sigma_{12}^{03}-K_{11}\sigma_{11}^{03}-K_{22}\sigma_{22}^{03}\Big)/$$

$$\Big(\chi_1 K_{11}\sigma_{11}^{03}+\chi_2 K_{22}\sigma_{22}^{03}\Big)\Big], \quad (50)$$

where

$$\eta=(\pi/6)\rho\Big(\chi_1 K_{11}\sigma_{11}^{03}+\chi_2 K_{22}\sigma_{22}^{03}\Big). \quad (51)$$

Then eq. (45) can be expressed as

$$P/\rho kT=P^{c}/\rho kT+P_1^{*}\Big(\lambda/\sigma^{0}\Big), \quad (52)$$

where

$$P_1^{*}=3\sqrt{2}\,\eta_0\Big[\Big(1+\eta_0-\eta_0^2/2\Big)/(1-\eta_0)^4\Big]F^{1}(K_0)E \quad (53)$$

is the first order quantum correction coefficient.

To test the theory, we first calculate the equation of state $P/\rho kT$ of the equimolar classical HGO fluid mixture for $\sigma_{11}^0=\sigma_{22}^0$ and $\nu_1=\nu_2$ using Eq (8).The calculated results are compared with the'exact' simulation data [6] in Table 3. The agreement is good . The values of the coefficient $P^*_1$ for the equimolar HGO mixture is given in Table 4. They are positive and increase with $\eta$ .

**Table 3.** The equation of state $P^{c}/\rho kT$ , of the equimolar classical HGO mixtures under different conditions

| Conditions | $\eta$ | $P^{c}/\rho kT$ | | | |
|---|---|---|---|---|---|
| | | $K_{11}/K_{22}$=1.792/1.0 | | $K_{11}/K_{22}$=1.792/1.436 | |
| | | Theory | Exact | Theory | Exact |
| $\sigma_{11}^0=\sigma_{22}^0$ | 0.30 | 4.13 | 4.20 | 4.10 | |
| | 0.45 | 9.80 | 10.15 | 9.68 | |
| $\nu_1=\nu_2$ | 0.30 | 4.19 | 4.25 | 4.23 | 4.80 |
| | 0.45 | 9.97 | 10.27 | 10.08 | 10.52 |

**Table 4.** The first order quantum correction coefficient $P_1^*$ for equimolar HGO mixture

| Conditions | | $P_1^*$ | |
|---|---|---|---|
| | | $K_{11}/K_{22}$=1.792/1.0 | $K_{11}/K_{22}$=1.792/1.436 |
| $\sigma_{11}^0=\sigma_{22}^0$ | 0.10 | 0.891 | 0.631 |
| | 0.20 | 3.077 | 2.178 |
| | 0.30 | 8.375 | 5.927 |
| | 0.40 | 21.758 | 15.399 |
| $\nu_1=\nu_2$ | 0.10 | 0.639 | 0.664 |
| | 0.20 | 2.217 | 2.293 |
| | 0.30 | 6.066 | 6.245 |
| | 0.40 | 15.870 | 16.241 |

**Table 5.** Percentage contribution of the quantum correction to the pressure $100\times(P-P^{c})/P$, for equimolar HGO mixture.

| | $\sigma_{11}^0=\sigma_{22}^0$ | | | |
|---|---|---|---|---|
| | $K_{11}/K_{22}$ 1.792/1.0 | $K_{11}/K_{22}$ 1.792/1.436 | $K_{11}/K_{22}$ 1.792/1.0 | $K_{11}/K_{22}$ 1.792/1.436 |
| 0.20 | 11.08 | 8.13 | 8.11 | 8.36 |
| 0.30 | 16.88 | 12.63 | 12.66 | 12.84 |
| 0.40 | 23.14 | 17.70 | 17.76 | 17.93 |

We have calculated the equation of state $P/\rho kT$ , for the equimolar HGO mixture for a range of $\eta$ at $\lambda/\sigma^0=0.0$ and 0.1 ( $\lambda/\sigma^0=0.0$ corresponds to the classical values). These values are shown in Figure 2 for $\sigma_{11}^0=\sigma_{22}^0$ and $K_{11}/K_{22}=1.792/1.0$ as a function of $\eta$ . In Table 5,we compare the percentage contribution of quantum correction to the pressure of equimolar HGO fluid mixture for $\lambda/\sigma^0=0.1$ .The percentage contribution depends on the condition as well as value of the shape parameters K. It also increases with of h.

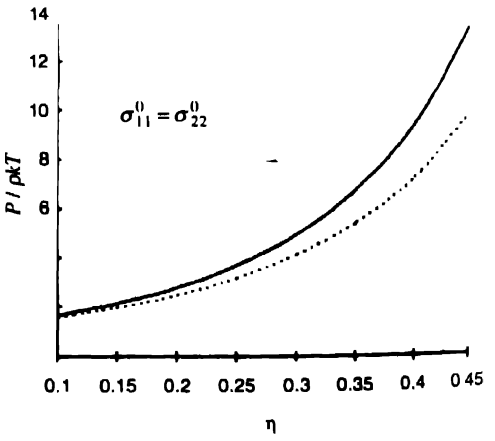


**Figure 2.** The equation of state $P/\rho kT$ for equimolar HGO mixture as function of $\eta$ for $K_{11}/K_{22}$ = 1.792/1.0 at $\lambda/\sigma^0$ = 0.0 and 0.1 $\lambda/$ corresponds to the classical values. The symbols are same as Figure 1.

## 5. Conclusion

The purpose of present paper is to calculate the quantum correction to the third virial coefficient and equation of state of the fluid mixture of the HGO molecules under two conditions, namely (i) The molecules of both species have same diameter and (ii) the molecules of both species have the same volume From the studies, we come to conclusion that the quantum effects depends on conditions.

### Refrences

[1] C G Gray and K E Gubbiss *Theory of Molecular Fluids* **Vol.1** (Clarendon · Oxford) (1984)

[2] Y Singh and S K Sinha *Phys Rep* **79** 213 (1981)

[3] T P Singh, J P Sinha and S K Sinha *Pramana - J Phys.* **31** 289 (1988)

[4] R Kumari and S K Sinha *Physica* **A211** 43 (1994)

[5] B J Berne and P Pechukas *J Chem. Phys.* **56** 4213 (1972)

[6] T Boublik and I Nezbeda *Colln Czeck. Chem Commun* **51** 2301 (1986)

[7] S A Rice and P Gray *The Statistical Mechanics of Simple Liquids* (New York. Interscience) (1965)

[8] U N Singh and S K Sinha *J Chem. Phys* **77** 5784 (1982)